Section: 3 Revision: 1 Date: 01/01/07 Page: 1 of 22

# SECTION 3 GUIDELINES FOR DEVELOPMENT OF MONITORING QUALITY SYSTEMS

Site specific NATTS monitoring plans and associated QA program elements for field and laboratory efforts, as approved by EPA, are designed to ensure data comparability across the entire NATTS Program network. The guidance in this section is a resource for EPA regional, state, local, and tribal field and laboratory staff to use in developing and approving specific plans for monitoring and QA that meet NATTS Program requirements, with references to complete documents.

## 3.0 QUALITY ASSURANCE

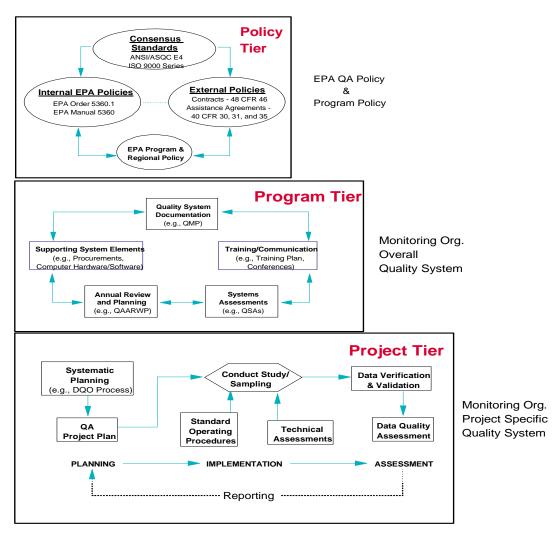
A quality system provides a framework for planning, implementing, assessing and reporting work performed by an organization and for carrying out QA procedures and QC activities. All EPA air monitoring programs include a QA component.

The EPA process for developing quality systems is illustrated in Figure 3.0-1. The EPA QA policy (top tier) provides the requirements and framework for a consistent development of quality systems in order to produce data of adequate quality for decision making.

At the program level a quality management plan (QMP) is developed for a specific organization such as EPA headquarters, the EPA regions, or a state, local or tribal monitoring organization. In addition, a QMP could also be developed to describe the quality system of a major monitoring program, such as the NATTS.

The project level (lowest tier) is where specific projects are implemented and shows how the quality of those data is controlled and assessed to meet specific program objectives.

Section: 3 Revision: 1 Date: 01/01/07 Page: 2 of 22



**Defensible Products and Decisions** 

Figure 3.0-1. EPA Quality System

The following paragraphs describe the program- and project-specific tiers of the quality system for the NATTS and local scale project grants and the responsibilities of EPA headquarters, the EPA regions and the state, local and tribal monitoring organizations.

## 3.1 PROGRAM TIER REQUIREMENTS

The program tier requirements direct development of the QMP for a specific organization or particular program. EPA policy requires that state, local, or tribal government agencies

Section: 3 Revision: 1 Date: 01/01/07 Page: 3 of 22

receiving financial assistance under the authority of 40 CFR Parts 31 and 35 are required to develop a QMP, which is implemented by the organization's executive leadership to:

- Document the organization's quality policy;
- Describe the organization's quality system; and
- Identify the organization's environmental programs to which the quality system applies.

The elements included in the QMP follow:

- 1. Management and Organization
- 2. Quality System and Organization
- 3. Personnel Qualifications and Training
- 4. Procurement of Items and Services
- 5. Documents and Records

- 6. Computer Hardware and Software
- 7. Planning
- 8. Implementation of Work Processes
- 9. Assessment and Response
- 10. Quality Improvement

Guidance and requirements for QMP development can be found on the EPA Quality Staff Home Page (*Quality Management Plan and Data Quality Objectives Development*, available at <a href="http://www.epa.gov/quality1/">http://www.epa.gov/quality1/</a>).

*NATTS Program QMP*. Since the NATTS program has specific objectives that are dependent on obtaining consistent and high quality data across the nation, EPA headquarters has assumed responsibility for the development of the QMP for this program. Similarly to the PM<sub>2.5</sub> speciation QMP, the NATTS QMP provides a set of minimum requirements that will be followed by all monitoring organizations participating in the NATTS. The QMP will cover only the technical elements applicable to the program and will not supersede a state, local or tribal monitoring organization's QMP. The Office of Air Quality Planning and Standards (OAQPS) began development of the NATTS QMP in 2002 and submitted it for review to the major program stakeholders. However, in 2003 OAQPS was provided with additional resources to implement a more comprehensive quality system. The OAQPS QA team completed revisions to

Section: 3 Revision: 1 Date: 01/01/07

Page: 4 of 22

the QMP using these additional resources and submitted the QMP for review in 2004. The final approved QMP was released in 2005.

# 3.2 PROJECT TIER REQUIREMENTS

This section describes the major stages of planning, implementing, assessing and reporting for the NATTS and local scale projects grants programs. The following project tier requirements, as illustrated in Figure 3.0-1, are addressed:

- DQOs; and
- QAPPs.

The following activities are incorporated into the QAPP:

- Standard operating procedures (SOPs);
- Technical assessments;
- Data verification/validation; and
- Data quality assessments (DQAs).

The project tier starts with the development of DQOs, which basically identify the level of uncertainty the user is willing to accept in the data from which decisions will be made. The project tier then proceeds with the development of a QAPP, which describes the quality system to assess and control the data quality to acceptable levels.

To understand the uncertainty that is involved with the data and to ensure that this uncertainty is within the limits defined by the DQOs, data quality indicators (DQIs) are identified (precision, bias, detectability, completeness) and measurement quality objectives (MQOs) or acceptance criteria are established for the overall program and through the phases of the program as necessary.

Section: 3 Revision: 1 Date: 01/01/07

Page: 5 of 22

## 3.2.1 NATTS DQOs

The DQO process provides a general framework for ensuring that the data collected by EPA meet the needs of decision makers and data users. The process establishes the link between the specific end use(s) of the data with the data collection process and the data quality (and quantity) needed to meet the program's goals. The result of the DQO process is a series of requirements used as the basis for the detailed planning in a project-specific QAPP. An appropriate DQO for the trends objective of the National Air Toxics Monitoring Program is:

To be able to detect a 15% difference (trend) between two successive 3-year annual mean concentrations within acceptable levels of decision error.

Being able to detect this trend would allow evaluation of the effectiveness of HAP reduction strategies. This is not to say that the NATTS data cannot be used for other purposes. However, the development of the NATTS quality system, DQIs (precision, bias, completeness), and their resultant MQOs were based upon detecting the trend above.

Since it would not be feasible to develop DQOs for every toxic compound measured in the NATTS, and it was a goal to establish as much simplicity and consistency in the MQOs as possible, the highest risk drivers were selected for the development of the DQOs: benzene, 1,3-butadiene, arsenic, hexavalent chromium, acrolein, and formaldehyde. A detailed document on the development of DQOs for the NATTS can be found in Attachment 3-1 to this section.

In summary, based on variability and uncertainty estimates from the pilot cities study, the specified air toxics trends DQOs should be met for monitoring sites that satisfy the specifications of:

• 1-in-6 day sampling frequency with at least an 85% quarterly completeness;

Section: 3 Revision: 1 Date: 01/01/07 Page: 6 of 22

- measurement precision controlled to a coefficient of variation (CV) of no more than 15%; and
- measurement detectability consistent with that described for each method or analytical approach presented in Section 4.0 of this document.

# 3.2.2 QAPP Development

As with the QMP, QAPPs are required for any environmental data operation using EPA funds. The purpose of the QAPP is to document planning results for environmental data operations and to provide a project-specific "blueprint" for obtaining the type and quality of environmental data needed for a specific decision or use. The QAPP documents how QA and QC are applied to an environmental data operation to assure that the results obtained are of the type and quality needed and expected to meet the program specific DQOs. All aspects of planning implementation, assessment and reporting described in Figure 3.0-1 should be discussed in the QAPP.

The NATTS participants are required to develop QAPPs for their monitoring organization. To provide consistency in the development of the quality system, the OAQPS QA team developed a model QAPP that was distributed to the NATTS managers in late 2002. This document was designed and written to be a guide for the NATTS managers to develop their individual QAPPs for their projects. The EPA regional offices are required to review and approve these QAPPs. However, it must be noted that review must specifically consider whether the plan will allow the NATTS program DQOs to be met, and not just whether a good technical approach is being proffered, before plan approval is provided. The NAATS DQOs take precedent over any regional, state, local, or tribal objectives. The most valuable resource for preparation of a site-specific QAPP is EPA's QA guidance document, *Model Quality Assurance Project Plan for the National Air Toxics Trends Stations*. (Available at http://www.epa.gov/ttn/amtic/files/ambient/airtox/nattsqapp.pdf).

This document represents a model QAPP for the NATTS. The OAQPS staff developed this model QAPP as an example of the type of information and detail necessary for the

Section: 3 Revision: 1 Date: 01/01/07 Page: 7 of 22

documents that will be submitted by state, local, or tribal air toxics monitoring programs involved in the NATTS. This model QAPP was generated using the EPA QA regulations and guidance as described in EPA QA/R-5, *EPA Requirements for Quality Assurance Project Plans*, and the accompanying document, EPA QA/G-5, *Guidance for Quality Assurance Project Plans*. All pertinent elements of the QAPP regulations and guidance are addressed in the model QAPP. Chapter 7 of the model QAPP describes the DQOs for the NATTS. Since all NATTS will be part of the trends network, OAQPS requires that the DQOs be identical. The SOPs listed in the table of contents of the model QAPP are a guidance document developed for OAQPS for the NATTS. This TAD was developed by Eastern Research Group, Morrisville, NC, and is available at the following Internet web site: <a href="http://www.epa.gov/ttn/amtic/airtxfil/html">http://www.epa.gov/ttn/amtic/airtxfil/html</a>.

## 3.2.3 SOPs

The National Toxics Monitoring Program proposes to use the performance-based measurement system (PBMS) concept:

As long as the quality of data the program needs (DQOs) is defined, the DQIs are identified, and the appropriate MQOs that quantify the data quality are met, any sampling/analytical method that meets these data quality requirements should be appropriate to use in the program.

The PBMS approach states that if the methods meet the data quality acceptance criteria, the resulting data are "comparable" and can be used in the program. Therefore, the quality system will continue to strive for the development of DQIs and MQOs to judge data quality and comparability and allow program managers to determine whether or not to require the use of a particular method (assuming this method meets the data quality needs). However, PBMS puts a premium on up-front planning and a commitment from monitoring organizations to adhere to the PBMS approach in implementing QC requirements.

Section: 3 Revision: 1 Date: 01/01/07 Page: 8 of 22

To ensure nationally consistent data of adequate quality (meeting the DQOs), the methods selected must consider the following DQIs:

- Detectability—being able to measure the concentration ranges required for the program;
- Completeness—being able to collect the quantity of data necessary without a high level of maintenance;
- Precision—being repeatable to an acceptable level; and
- Bias—being able to maintain a concentration that does not systematically deviate from the true concentration.

Currently, there are only a few sampling and analytical methods available that meet the DQOs for the NATTS. Section 4 of the NATTS TAD provides strongly suggests guidance for the consistent use of sampling and analysis methods for the NATTS. Through QAPP reviews and technical systems audits (TSAs), significant deviations that could affect the quality of the data will be identified and discussed to ensure that the methods will meet the DQOs. (Documentation related to the development of NATTS DQOs is included in Attachment 3-1 to this section.)

As part of the QAPP development process, NATTS participants are required to develop SOPs with details specific to their environmental data operations. As an example, it is not appropriate to simply reference EPA Toxic Organic (TO) Compendium Method 15 in the QAPP as the method for use since there are a number of options included in that method from which any organization would have to select the specific option used for their procedure.

If subcontractors are used by the NATTS monitoring organization, they must submit their SOPs to the NATTS monitoring organization for incorporation into the QAPP prior to EPA regional office review and approval.

Section: 3 Revision: 1 Date: 01/01/07 Page: 9 of 22

# 3.2.4 Technical Assessments

An assessment is an evaluation process used to measure performance or effectiveness of a system and its elements. Assessment is an all-inclusive term used to denote audits, performance evaluations, proficiency tests, management systems audits, peer review, inspection, or surveillance.

The following paragraphs outline the components of the NATTS technical assessments. Due to the one-year duration of local scale projects grants, it is not anticipated that external technical systems audits would be performed on the monitoring activities of these grants. The laboratory technical systems audits, proficiency tests, and calibration certification will be made available only if the laboratories used in the local scale projects happen to be participating in the NATTS program; otherwise the local scale projects will not be included in these external assessment activities. These assessments could be made available if the timing of grant activity could be coordinated with funding and planning for these assessments for the NATTS.

*TSAs*—A TSA is a thorough, systematic, on-site, qualitative audit of facilities, equipment, personnel, training, procedures, recordkeeping, data validation, data management, and reporting aspects of a quality system.

- Laboratory TSA—EPA, using contractors and EPA regional offices, will attempt to perform 12 audits a year of the laboratories performing analysis for the NATTS. It is expected that audits of all laboratories would be completed in two years. An audit check sheet will be developed to provide a consistent evaluation across all laboratories. Reports on these audits will be included in an annual QA report.
- **Field TSA**—The EPA regional offices will perform TSAs on field activities during their normal TSA audit schedules.
- **Internal TSA**—Monitoring organizations as part of the internal quality system procedures may perform technical systems audits of the environmental data operations as described in their QAPP.

Section: 3 Revision: 1 Date: 01/01/07 Page: 10 of 22

**Proficiency Tests (PT)** —A PT is a type of assessment in which a sample, the composition of which is unknown to the analyst, is provided to test whether the analyst/laboratory can produce analytical results within the specified acceptance criteria. OAQPS presently uses PT studies for the NATTS program laboratories using the following process:

- Decide on the **audit constituents** and the **concentration levels**:
- Use an independent organization to develop the PT samples. The organization (vendor) that creates the PT samples does not perform analysis for any of the NATTS state or local agencies;
- The independent organization/vendor certifies the audit concentration and constituents.

Calibration Cylinder Certification—OAQPS, in conjunction with Office of Radiation and Indoor Air (ORIA) laboratory in Las Vegas, NV, hope to be implementing a program in which the VOC calibration cylinders will be sent from the NATTS analytical laboratories to ORIA for certification. In the future, OAQPS may perform a national purchase of calibration cylinders and certify their concentration prior to use by the laboratories.

Through-the-Probe Performance Evaluation—Since 2001, OAQPS has been reinventing the mailable National Performance Evaluation Program to a through-the-probe audit activity for the criteria pollutants. Trailers and/or mobile laboratories visit a monitoring site and challenge the monitors with audit gases through the inlet instead of the back of the monitor. OAQPS is augmenting the current program trailers/laboratories with the equipment to provide similar audits to the NATTS sites for VOCs and aldehydes.

# 3.2.5 Verification and Validation

Verification is confirmation by examination and provision of objective evidence that **specified requirements** have been fulfilled. Validation is confirmation by examination and

Section: 3 Revision: 1 Date: 01/01/07 Page: 11 of 22

provision of objective evidence that the particular requirements **for a specific intended use** are fulfilled. It is the responsibility of the state, local and tribal monitoring organizations and their contractors that operate, collect and analyze the samples to perform the data validation and verification of the data before submission to the AQS national data base. The procedures for validation and verification should be detailed in their QAPPs and therefore reviewed by the EPA regional offices.

In addition, the VOCDat software tool, which is free and available to the public, was developed through EPA funding. This tool can be used to validate data and get the data into a format that can be sent to the AQS. [VOCDat is available at <a href="http://www.sonomatech.com/sti/software\_projects\_vocdat.htm">http://www.sonomatech.com/sti/software\_projects\_vocdat.htm</a>.]

Due to the fact that the DQOs (a specific intended use) have been identified, OAQPS, with the help of the EPA regions and NATTS stakeholders, can develop consistent data verification and validation criteria similar to the validation templates developed for the PM<sub>2.5</sub> program. OAQPS will incorporate the verification/validation templates into the quality management plan expected for completion in 2004.

# 3.2.6 DQAs and Reporting

A DQA is used to determine whether the type, quantity, and quality of data needed to support a decision (the DQO) have been achieved.

OAQPS will hire a contractor to create a quality assurance annual report (QAAR). The QAAR will document the information on the DQIs and independent assessments (TSAs, PTs, certifications) that are performed within a calendar year. These results will then be compared against the MQO criteria for this program. The annual report will be used by OAQPS, EPA regional offices, and NATTS stakeholders to assess the status of the program. If problems are identified, corrective steps by the NATTS state and local agencies with the input of the EPA regional offices will be undertaken.

Section: 3 Revision: 1 Date: 01/01/07 Page: 12 of 22

After the first three years of NATTS monitoring, a more interpretive DQA will be performed to determine whether the assumptions and data quality requirements used to develop the DQOs are being achieved.

Section: 3 Revision: 1 Date: 01/01/07 Page: 13 of 22

# 3.3 QUALITY SYSTEM DEVELOPMENT FOR THE TOXICS PROGRAM

The Science Advisory Board, results from 1996 NATA analyses, and the national data analysis project completed in 2001 suggest that the National Toxics Monitoring Program needs to develop and administer a quality system with the goal of producing data of adequate quality. The objective of the National Toxics Monitoring Program quality system is to identify the tolerable levels of uncertainty and implement mechanisms for the control and assessment of data quality to maintain uncertainty within these tolerable levels.

Figure 3.3-1 provides a simple paradigm for development of a quality system for a monitoring program. The term "uncertainty" is used generically to describe the sum of all sources of error associated with a given portion of the measurement system. Overall data uncertainty is the sum of total population uncertainty and total measurement uncertainty. Population uncertainty is defined as the natural spatial and temporal variability in the population of the data being evaluated and is identified by the DQI called representativeness. Total measurement uncertainty is the total error associated with the data collection operation and is defined by the DQIs: precision, bias completeness, comparability and detectability. As Figure 3.3-1 illustrates, development of the quality system involves three stages:

- **Formulation of the DQOs** to define the quality of data needed to make a correct decision an acceptable percentage of the time. Section 3.2.1 provides a description of the DQOs. The quality is defined through quantification of the **DQIs**;
- **Formulation of MQOs** to identify the number and type of QC samples with the acceptance criteria for those samples so that the user can control and assess the quality of the data;
- **Performance of DQAs** to determine by statistical assessment if the DQOs are met and to provide descriptions of data uncertainty. If the DQOs are not met, the DQAs would help to determine whether modifications to the DQOs are necessary or more QC is required. The DQAs are briefly described in Section 3.2.6.

Section: 3 Revision: 1 Date: 01/01/07 Page: 14 of 22

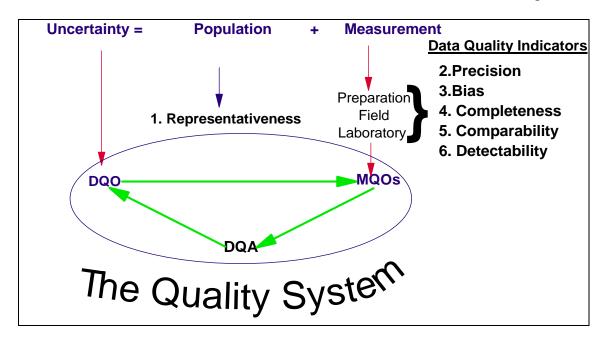


Figure 3.3-1. Quality System for the Toxics Program

## 3.3.1 DQIs

Controlling and assessing data quality to achieve the DQOs requires the ability to define the appropriate DQIs and identify measurements that can be made to provide estimates of these indicators. In addition, these DQIs can be used as metadata elements in a comprehensive data base. The important DQIs include:

Representativeness—Representativeness is a measure of the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. The current NATTS network has been based on a number of logistical and resource constraints that has limited its size to ~22 sites. In addition, since there have been some constraints on how these sites were identified, the personnel developing the NATTS made the assumption that these sites accurately and precisely represent a characteristic of the population necessary to determine a national trend. During the development of the DQOs, the NATTS pilot data were used to provide measurements of population parameters. To achieve the NATTS DQOs, a sampling frequency of one day in six was required.

Section: 3 Revision: 1 Date: 01/01/07 Page: 15 of 22

**Precision**—Are the data collection approaches repeatable? This step is important for determining whether the measurement system is under control. The estimate of precision (and bias) must be inclusive of the total data collection system, i.e., the estimate should include imprecision related to field, preparation, handling and laboratory operations. Precision will be assessed through the use of duplicate or collocated sampling, duplicate filters and a number of laboratory techniques. To achieve the NATTS DQOs, total precision should be controlled to <15% CV.

**Bias**—Is there a systematic deviation from the true concentration being reported? Bias will be assessed through the operation of a proficiency testing program and standards certifications which will provide assessments of laboratory bias issues. Field through-the-probe and laboratory performance audits will also be conducted as the approach/procedures/equipment to accomplish this effort are developed.

**Completeness**—Is enough information being collected to ensure confidence in the conclusion or decisions made with the data? To achieve the NATTS DQOs, a completeness level of 85% or greater is required.

**Sensitivity**—Do the management activities allow quantification, with the appropriate level of certainty, of a significant (acceptable) number of values from a monitoring site? Target minimum Method Detection Limits (MDLs) have been established for the NATTS program and are presented with each method in Section 4.0 of this document.

**Comparability**—Do the data from one site compare to the data from another site and across the nation? This comparability is achieved by setting DQOs and establishing the correct MQOs for the DQIs above. If the acceptance criteria are achieved, the data should be comparable.

Section: 3 Revision: 1 Date: 01/01/07 Page: 16 of 22

## 3.3.2 MQOs

MQOs are identified to control and assess various elements of a data collection activity and provide the sample used to estimate some of the DQIs above. Thorough the implementation of MQOs and achieving the acceptance limits for those MQOs, the assumption can be made that the DQOs will be met.

The highest risk drivers selected for the development of the DQOs include the following compounds:

- Benzene, 1,3-butadiene, and acrolein (VOCs, analyzed by gas chromatography/mass spectrometry/Selective Ion Monitoring (GC/MS/SIM));
- arsenic (a metal, analyzed by inductively coupled plasma/mass spectrometry (ICP/MS));
- hexavalent chromium (a metal, analyzed by ion chromatography (IC)); and
- formaldehyde (carbonyl compounds, analyzed by high performance liquid chromatography (HPLC)).

MQOs for these compounds are summarized in Tables 3.3-1, 3.3-2, 3.3-3, and 3.3-4.

Table 3.3-1. VOC MQOs for the NATTS Program: Benzene, 1,3-butadiene, and Acrolein

MQO Parameter	Requirement	Acceptance Criteria
Precision	Duplicate samples or Collocated samples. Duplicate samples are taken simultaneously through the same collection system. Collocated samples are taken simultaneously through 2 separate collection systems at the same location.  10 % of total samples – 6 per year for 1-in-6 day sampling.	<15% CV
Bias	Performance Evaluation samples. 1 per calendar quarter if samples are available.	<20% CV per analyte
Completeness	Valid samples collected compared to samples planned.	>85%

Section: 3 Revision: 1 Date: 01/01/07 Page: 17 of 22

Table 3.3-2. Metals MQOs for the NATTS Program: Arsenic

MQO Parameter	Requirement	Acceptance Criteria
Precision	Collocated samples. Collocated samples are taken simultaneously through 2 separate collection systems at the same location.  10 % of total samples – 6 per year for 1-in-6 day sampling.	<15% CV
Bias	Performance Evaluation samples. 1 per calendar quarter if samples are available.	<20% CV per analyte
Completeness	Valid samples collected compared to samples planned.	>85%
Sensitivity	Experimentally determined Method Detection Limit conducted per the specifications of 40 CFR Part 136, Appendix B. Determined annually, or after any major instrument change.  Minimum of 7 low level filters analyzed over a 2-day period (minimum).	arsenic: 0.0221 ng/m <sup>3</sup>

Table 3.3-3. Hexavalent Chromium MQOs for the NATTS Program: Hexavalent Chromium

MQO Parameter	Requirement	Acceptance Criteria
Precision	Collocated samples. Collocated samples are taken simultaneously through 2 separate collection systems at the same location.  10 % of total samples – 6 per year for 1-in-6 day sampling.	<15% CV
Bias	Performance Evaluation samples. 1 per calendar quarter if samples are available.	<20% CV per analyte
Completeness	Valid samples collected compared to samples planned.	>85%
Sensitivity	Experimentally determined Method Detection Limit conducted per the specifications of 40 CFR Part 136, Appendix B. Determined annually, or after any major instrument change.  Minimum of 7 low level filters analyzed over a 2-day period (minimum).	hexavalent chromium: 0.011 ng/m <sup>3</sup>

Section: 3 Revision: 1 Date: 01/01/07 Page: 18 of 22

Table 3.3-4. Carbonyl Compounds MQOs for the NATTS Program: Formaldehyde

MQO Parameter	Requirement	Acceptance Criteria
Precision	Duplicate samples or Collocated samples. Duplicate samples are taken simultaneously through the same collection system. Collocated samples are taken simultaneously through 2 separate collection systems at the same location.  10 % of total samples – 6 per year for 1-in-6 day sampling.	<15% CV
Bias	Performance Evaluation samples. 1 per calendar quarter if samples are available.	<20% CV per analyte
Completeness	Valid samples collected compared to samples planned.	>85%
Sensitivity	Experimentally determined Method Detection Limit conducted per the specifications of 40 CFR Part 136, Appendix B. Determined annually, or after any major instrument change.  Minimum of 7 low level cartridge standards analyzed over a 2-day period (minimum).	formaldehyde: $0.007 \mu g/m^3$

To help in achieving NATTS MQOs, there are many method specific technical specification/criteria for both sample collection and analysis that should be adhered to as closely as possible. Summaries of suggested technical specifications/criteria are presented in Tables 3.3-5, 3.3-6, 3.3-7

Table 3.3-5. Suggested Technical Specifications/Criteria for VOC Measurements: Benzene, 1,3-Butadiene, and Acrolein

Parameter	Requirement	Acceptance Criteria Detail and Flag
Field Sampling		
Sampler Certification Challenge	Representative selection of analytes at a typical/practical level at ~20% relative humidity (RH). Performed prior to field deployment and/or after any major component repair.	± 20% per analyte
Sampler Certification Zero	Zero air at ≥20% RH. Performed prior to field deployment and/or after any major component repair.	≤0.2 ppbv¹ per analyte or MDL, whichever is greater
Sampling Period	24 hours ± 5%	

Section: 3 Revision: 1 Date: 01/01/07 Page: 19 of 22

Table 3.3-5. Suggested Technical Specifications/Criteria for VOC Measurements: Benzene, 1,3-Butadiene, and Acrolein

Parameter	Requirement	Acceptance Criteria Detail and Flag
Canister Cleanliness	One canister per batch cleaned	≤0.2 ppbv per analyte or MDL,
Certification	1	whichever is greater
Analysis		-
Holding Time (Days)	30 days from sampling	
MS Tune Check	Daily or every 24 hours	Meets Method TO-15 criteria (Table
(4-bromofluorobenzene)		3)
Initial Calibration Levels	Multipoint calibration:	RSD of response factor ≤ 30%
Frequency	5 or 6 points, ranging from 0.25 to 15	RRT for analytes ± 0.06 retention time
	ppbv	units from mean retention time in
	At least quarterly or after failure to	multipoint calibration
	meet acceptance criteria or after major	
	change in instrumentation.	
Continuing Calibration Check	Daily	± 30% bias from mean response factor
Frequency		from multipoint calibration
Laboratory System Blank	Clean canister filled with humidified air	≤ 0.2 ppbv per analyte or MDL,
Frequency	Daily, prior to sample analysis	whichever is greater
Analysis		
Laboratory Control Sample	Second Source Standard	Recovery limits 70 to 130%
Frequency	Daily	
Internal Standards Frequency	Every standard, blank, and sample	Area response within ± 40% of most
		recent calibration check
		Retention time ± 0.33 min of most
		recent calibration check
Duplicates Laboratory	Replicate laboratory analysis of	< 30% relative percent difference for
Frequency	duplicate or collocated field samples	analytes $> 5 \times MDL$

Table 3.3-6. Suggested Technical Specifications/Criteria for Metals Measurements: Arsenic

Parameter	Requirement	Acceptance Criteria
Field Sampling		
Sampling Period	24 hours ± 5%	
Glassware/Plasticware	Washed in 1:1 nitric acid in a clean	
Preconditioning	room, double-wrapped in sealed	
	plastic bags.	
Filter Type: Quartz	1 per filter lot change	
Field Blanks	1 per 10 filters or 10%	
Analysis		
Holding Time	180 days, stored at 15 to 30 °C	
Reporting Units	Total ng or ng/m <sup>3</sup>	
Extraction Efficiency	Using NIST Standard Reference	75 to 125%
	Material	
MS Tune Check	Daily	
Initial Calibration Levels	Multipoint calibration daily	$r^2 > 95\%$
Frequency		
Initial Calibration Verification	Immediately after initial calibration	90 to 110% of the actual
		concentration

Section: 3 Revision: 1 Date: 01/01/07 Page: 20 of 22

Table 3.3-6. Suggested Technical Specifications/Criteria for Metals Measurements: Arsenic

Parameter	Requirement	Acceptance Criteria
Initial Calibration Blank	Immediately after initial calibration verification	< 0.046 ng/m <sup>3</sup>
High Standard Verification	Following the initial calibration blank analysis	95 to 105% of the actual concentration
Interference Check Standard	Following the high standard verification, every 8 hours, and at the end of a run	80 to 120% of the actual concentration
Continuing Calibration Check	Analyzed before the first sample, after every 10 samples, and at the end of the run	90 to 110% of the actual concentration
Analysis		
Continuing Clarification Blanks	Analyzed following each continuing calibration verification	$< 0.046 \text{ ng/m}^3$
Blanks		
Field Blank Frequency	One per sampling event	< MDL
Laboratory Reagent Blank Frequency	One per sample batch	< MDL
Laboratory Calibration Blank Frequency	Daily	< MDL
Laboratory Control Sample (NIST SRM) Frequency	Daily or 1 per sample batch	80% to 120% recovery
Matrix Spike	1 per sample batch	Recovery 75 to 125%
Serial Dilution	1 per sample batch	90 to 110% of undiluted sample

Table 3.3-7. Suggested Technical Specifications/Criteria for Hexavalent Chromium

Parameter	Requirement	Acceptance Criteria
Field Sampling	-	_
Collection Rotameter Calibration	Prior to system deployment and annually thereafter.	$R^2 \ge 0.9995$
Filter Preparation	Purity of reagents is critical	99.99% purity or better
Filter Background	Checked once per batch	
Filter Shipment	Ship cold, over Blue Ice	
Filter Storage	Store in freezer (-20 °C)	
Analysis		
Holding Time (Days)	Extraction: Within 21 days of sampling Analysis: Within 24 hours of extraction	
Initial Calibration Levels Frequency	Multipoint calibration with every sample batch. 0.1 to 2 ng/mL	$R^2 \ge 0.995$ Relative standard deviation $< 10\%$

Section: 3 Revision: 1 Date: 01/01/07 Page: 21 of 22

Table 3.3-7. Suggested Technical Specifications/Criteria for Hexavalent Chromium

Parameter	Requirement	Acceptance Criteria
Continuing Calibration Check	After every 10 <sup>th</sup> sample and at the	Within 10% of target value
Frequency	end of sample analysis.	
Blanks	10% of all samples (24 per year for	
Field Blank	1-in-6 day sampling).	< MDL
Frequency	Every batch.	< MDL
Laboratory Reagent Blank		
Frequency		
Performance Standards	Quarterly	≥ 85% recovery
Frequency		
Laboratory Control Sample	Second source standard.	± 10% of theoretical value
Frequency	Every batch of filters extracted.	
Method Spike	Every batch	± 20% of theoretical
Duplicate Laboratory Analyses	One for every collocated sample	$\pm$ 20% for all values $>$ 5 $\times$ MDL

Table 3.3-8. Suggested Technical Specifications/Criteria for Carbonyl Compounds: Formaldehyde

Parameter	Requirement	Acceptance Criteria
Field Sampling		
Sampler Certification	Zero air at ≥20% RH performed prior	< 0.2 ppbv for each analyte
Zero	to field deployment and after any	
	major component repair/replacement	
Cartridge Lot Blank Check	Minimum of 3 cartridges for each new	Formaldehyde <0.15 μg/cartridge
	lot	Acetaldehyde < 0.10 μg/cartridge
Field Blank	Frequency = 1 per calendar month	<0.15 μg formaldehyde
		<0.10 μg acetaldehyde
Analysis		
Holding Time (Days)	Preparation: 14 days from sample	
	collection (tube at 4 °C).	
	Analysis: 30 days from preparation	
	(extract at 4 °C).	
HPLC Column Efficiency	Determined at instrument setup and	Resolution between acetone hydrazone
	once per sample batch	and propionaldehyde hydrazone ≥ 1.0
		Column efficiency > 5,000 plate
		counts

Section: 3 Revision: 1 Date: 01/01/07 Page: 22 of 22

 ${\bf Table~3.3-8.~Suggested~Technical~Specifications/Criteria~for~Carbonyl~Compounds:} \\ {\bf Formal dehyde}$ 

Parameter	Requirement	Acceptance Criteria
HPLC Linearity Check	Performed at instrument setup and when calibration check fails to meet acceptance criteria.  Analyze a 5-point calibration curve and a second source QC sample in triplicate.	Correlation coefficient $\geq 0.999$ , relative error for each level against calibration curve $\leq 20\%$ relative error Intercept should be $\leq 10,000$ area counts per compound $(0.06~\mu g/\mu L)$
Retention Time Check	Once every 12 hours or less	Acetaldehyde, benzaldehyde, hexaldehyde within retention time window established by determining 3σ or ± 2% of the mean calibration and midpoint standards, whichever is greater
Initial Calibration Levels Frequency	Multipoint calibration: 6-point curve from 0.01 μg/mL to 3.0 μg/mL. Every six months or after major instrument change.	Correlation coefficient ≥ 0.999 Relative error for each level against calibration curve ≤ 20%
Continuing Calibration Check Frequency	Once every 12 hours	85 to 115% recovery
Calibration Accuracy	Second source standard, analyzed once after multipoint calibration, in triplicate	85 to 115% recovery
Laboratory Reagent Blank Frequency	Bracket sample batch	Formaldehyde: <0.4 µg/ml derivatized <0.3 µg/cartridge underivatized Measured concentration < 5 x MDL
Performance Standards Frequency	Once per quarter	85 to 115% recovery
Laboratory Control Sample Frequency	Second source standard Once every 12 hours after calibration check	85 to 115% recovery
Laboratory Duplicates Frequency	Replicate analyses of every duplicate field sample. 12 replicate analyses for 1-in-6 day sampling.	± 20% relative percent difference
Method Spike/Method Spike Duplicate <sup>4</sup>	One MS/MSD per batch of 20 samples	80 to 120% recovery for all compounds